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Citation for final published version:

Reed-Berendt, Benjamin G., Mast, Nicolas and Morrill, Louis C. ORCID: <https://orcid.org/0000-0002-6453-7531> 2020. Manganese-catalyzed one-pot conversion of nitroarenes into N-methylarylamines using methanol. *European Journal of Organic Chemistry* 2020 (9) , pp. 1136-1140. 10.1002/ejoc.201901854 file

Publishers page: <http://dx.doi.org/10.1002/ejoc.201901854>
<<http://dx.doi.org/10.1002/ejoc.201901854>>

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Manganese-Catalyzed One-Pot Conversion of Nitroarenes into *N*-Methylarylamines Using Methanol

Benjamin G. Reed-Berendt,^[a] Nicolas Mast,^[a] and Louis C. Morrill*^[a]

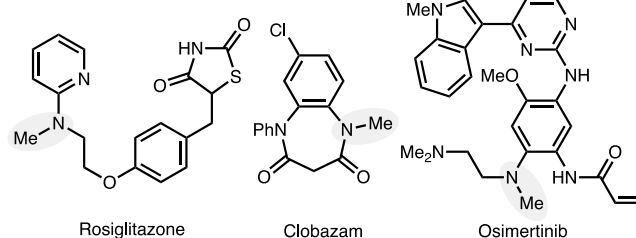
Abstract: A manganese-catalyzed one-pot conversion of nitroarenes into *N*-methylarylamines has been developed. This transfer hydrogenation method employs a well-defined bench stable Mn PN³P pincer precatalyst in combination with methanol as both the reductant and the C1 source. A selection of commercially available nitroarenes was converted into *N*-methylarylamines in synthetically useful yields.

Introduction

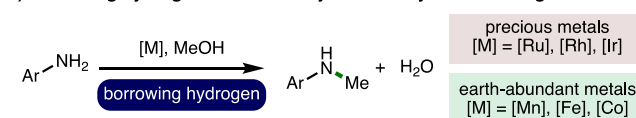
N-methylamines are an important structural motif that feature within a diverse array of useful compounds, including medicines, agrochemicals, dyes and surfactants.^[1] More specifically, *N*-methylarylamines can be found within a broad range of pharmaceuticals, including Rosiglitazone, Clobazam and Osimertinib (Scheme 1A). Traditional methods for *N*-methylation of arylamines include the use of hazardous reagents such as methyl iodide, dimethyl sulfate and diazomethane, which typically produce a mixture of mono- and di-methylated arylamines whilst generating stoichiometric quantities of waste.^[2] Reductive couplings of arylamines with carbon dioxide or formic acid can also be employed for *N*-methylation.^[3] Alternatively, the borrowing hydrogen approach^[4] enables methanol^[5] to be employed as the methylating agent for the selective mono-*N*-methylation of anilines (Scheme 1B).^[6]

Arylamines are commonly accessed *via* the catalytic reduction of commercially available and inexpensive nitroarenes.^[7] As such, synthetic methods that enable the formation of *N*-methylarylamines directly from nitroarenes are valuable. In this domain, reductive catalytic approaches employing formaldehyde, formic acid or carbon dioxide in combination with silanes or hydrogen gas have been reported.^[8] Alternative approaches include the photo-reductive *N*-methylation of aniline over Au-TiO₂^[9] and the reductive C-N cross coupling of nitroarenes and boronic acids by P(III)/P(V)=O catalysis.^[10] Methanol can be employed as both the reductant and the C1 source for the reductive methylation of nitroarenes. This attractive option, which avoids the use of expensive and/or hazardous reductants, has been developed using a variety of heterogeneous catalytic systems.^[11] Some of the aforementioned methods suffer from poor selectivity for mono- vs di-methylation, which somewhat diminishes the synthetic

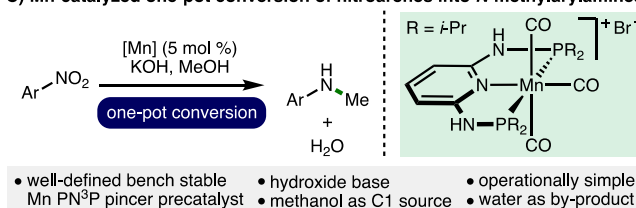
A) Examples of pharmaceuticals containing the *N*-methylarylamine motif



B) Borrowing hydrogen *N*-monomethylation of arylamines using methanol



C) Mn-catalyzed one-pot conversion of nitroarenes into *N*-methylarylamines



Scheme 1. Introduction.

utility. Recent advances have developed homogeneous precious metal catalyst systems based on Ru^[12] and Pd^[13] for the selective conversion of nitroarenes to *N*-methylarylamines using methanol, which exhibit good selectivity for mono-*N*-methylation. Despite these notable advances, the use of a catalyst based upon an earth-abundant first row transition metal for this useful transformation has not previously been reported. As part of our ongoing interest in (transfer) hydrogenation chemistry,^[14] herein we report the Mn-catalyzed^[15] one-pot conversion of nitroarenes into *N*-methylarylamines using methanol (Scheme 1C).^[16]

Results and Discussion

To commence our studies, the one-pot conversion of nitrobenzene **1** to *N*-methylaniline **2** was selected as the model system (Table 1). After extensive optimization,^[17] it was found that a catalytic system composed of the well-defined bench stable^[18] Mn PN³P pincer precatalyst **3** (5 mol %) introduced by Sortais and co-workers,^[19] and KOH (2 equiv.) as base in MeOH ([**1**] = 0.5 M) with 4 Å molecular sieves at 110 °C for 16 h gave **2** in 94% NMR yield and 90% isolated yield (entry 1). No conversion occurs in the absence of the manganese precatalyst **3** or KOH (entries 2 and 3). Interestingly, it was also found that the addition of 4 Å molecular sieves was crucial for reactivity (entry 4). Although the precise role of the 4 Å molecular sieves is not known at this stage, they may promote the transformation *via* nitroarene activation due to their acidic properties and/or by

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Information about the data that underpins the results presented in this article, including how to access them, can be found in the Cardiff University data catalogue under: <http://XXXX> (accessed XXXX)

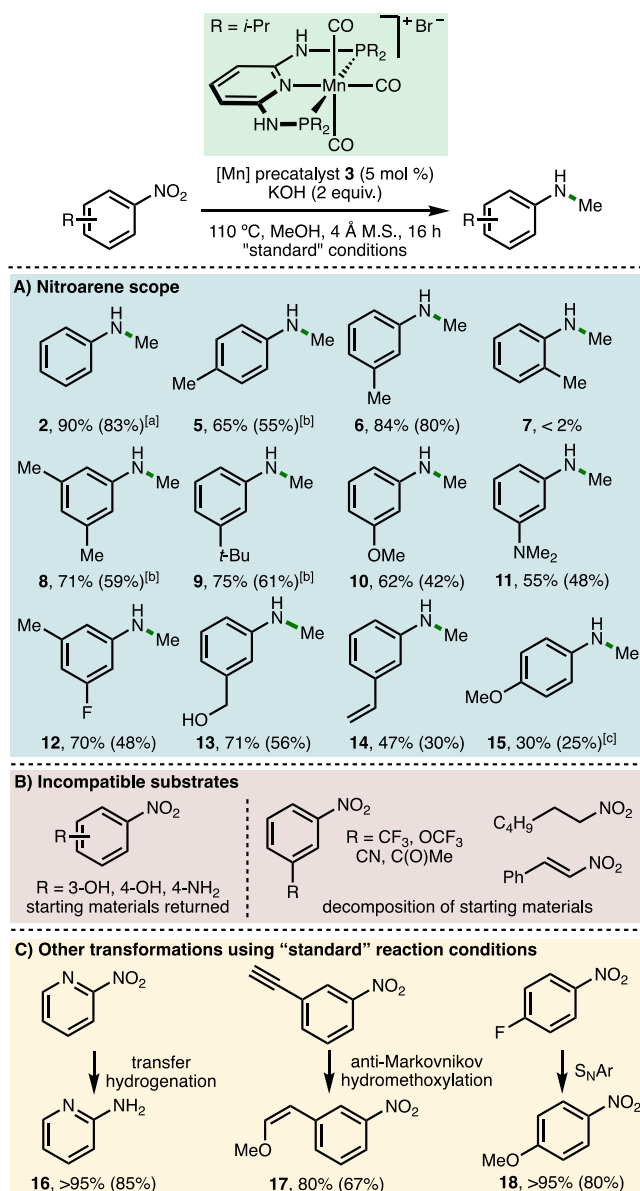
Table 1: Reaction Optimization.^[a]

Entry	Variation from "standard" conditions	Yield ^[b] (%)
1	none	94 (90)
2	no [Mn] precatalyst 3	< 2
3	no KOH	< 2
4	no 4 Å molecular sieves	< 2
5	[Mn] precatalyst 4 (5 mol %) instead of 3	14
6	NaOH (2 equiv.) instead of KOH	83
7	K ₂ CO ₃ (2 equiv.) instead of KOH	83
8	[1] = 1 M	33
9	80 °C	< 2
10	[Mn] precatalyst 3 (2.5 mol %)	74

[a] Reactions performed in a sealed tube using **1** (0.5 mmol) and synthesis grade MeOH. [1] = 0.5 M. [b] As determined by ¹H NMR analysis of the crude reaction mixture with 1,3,5-trimethylbenzene as the internal standard. Isolated yield given in parentheses.

sequestering water from the reaction media to perturb important equilibria (cf. Scheme 3C). Substitution of [Mn] precatalyst **3** with the alternative Mn PNP pincer precatalyst **4**^[20] resulted in only 14% conversion to *N*-methylaniline **2** (entry 5). When NaOH or K₂CO₃ were employed as the base, lower conversions to **2** was observed (entries 6 and 7). Furthermore, increasing the reaction concentration (entry 8), lowering the reaction temperature (entry 9) and reducing the precatalyst loading to 2.5 mol % (entry 10), all lowered the efficiency of the one-pot reductive methylation process.

With optimized reaction conditions in hand (Table 1, entry 1), the scope of the one-pot conversion of nitroarenes to *N*-methylarylamines was explored (Scheme 2). Firstly, the reductive methylation procedure performs well upon scale-up, with the formation of **2** successfully carried out on a 10 mmol scale in 83% isolated yield (0.89 g of **2**).^[21] Methyl substitution at the 2-, 3- and 4-positions of the nitroarene was investigated (Scheme 2A). It was found that 4- and 3-methyl substitution was tolerated, giving 65% and 84% conversion to the corresponding *N*-methylarylamines, respectively. However, incorporation of a 2-methyl substituent within the nitroarene resulted in complete recovery of the starting material after 16 h reaction time, which could be attributed towards the increased steric shielding of the nitro functionality causing inhibition of the transfer hydrogenation step. As product **6** was formed in the highest conversion from this series, other substitution at the 3-position within the nitroarene was subsequently explored. Gratifyingly, other alkyl (3,5-(CH₃)₂ and 3-*t*-Bu) groups in addition to methoxy,



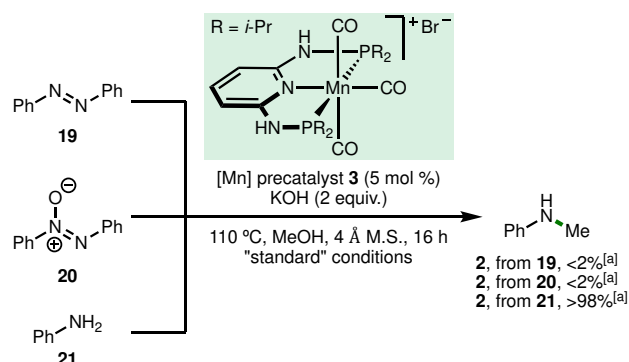
Scheme 2. Substrate Scope. Reactions performed in a sealed tube using 0.5 mmol of substrate and synthesis grade MeOH. Yields as determined by ¹H NMR analysis of the crude reaction mixture with 1,3,5-trimethylbenzene as the internal standard. Isolated yield given in parentheses. [a] 10 mmol of substrate, 24 h. [b] 72 h. [c] 130 °C.

dimethylamino, and fluoro substitution were all tolerated at the 3-position, accessing products **8–12** in synthetically useful yields. Furthermore, functional groups that can undergo (de)hydrogenation, including alcohols and alkenes, can be present within the nitroarene and are preserved within *N*-methylarylamines **13** and **14**. Modest conversion to **14** was observed despite full consumption of the nitroarene starting material, which was attributed to some decomposition of the nitroarene substrate and/or product **14** under the reaction conditions. 1-Methoxy-4-nitrobenzene was converted to product **15** in only 6% NMR yield using the standard reaction conditions, which increased to 30% when the reaction temperature was raised to 130 °C. The mass balance in both cases was

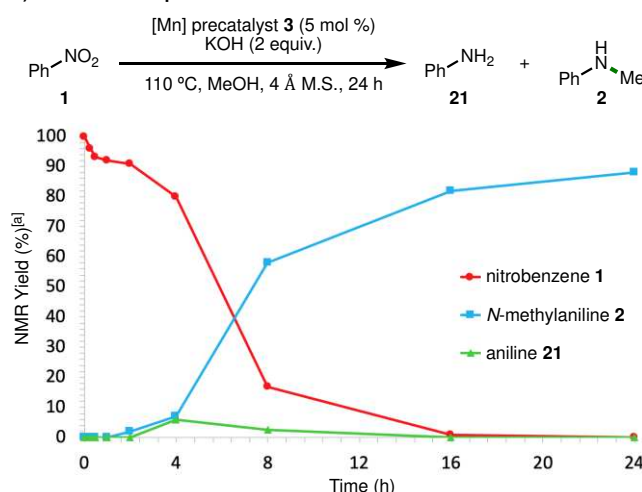
remaining starting material, which can be explained by the mesomeric effect of the methoxy group resulting in a more challenging transfer hydrogenation of the nitro functionality. A variety of alternative substrates containing nitro functional groups were incompatible with the optimized reaction conditions (Scheme 2B). It was found that nitroarenes containing hydroxyl or amino functionalities were unreactive, with starting materials returned. These substrates may inhibit catalysis *via* coordination to Mn and/or may be too electron rich to undergo transfer hydrogenation. Nitroarenes containing various electron-withdrawing groups at the 3-position, in addition to 1-nitrohexane and β -nitrostyrene, were each found to be incompatible with this protocol, with complex reaction mixtures obtained across a range of reaction conditions explored. However, when specific nitroarenes were subjected to the optimized reaction conditions, conversion to products other than *N*-methylarylamines was observed (Scheme 2C). For example, 2-nitropyridine underwent transfer hydrogenation to form 2-aminopyridine **16** in 85% isolated yield. The subsequent mono-*N*-methylation did not proceed, presumably due to the low nucleophilicity of arylamine **16**. A nitroarene containing an ethynyl substituent at the 3-position participated in an anti-Markovnikov hydromethoxylation^[22] reaction to give 80% conversion to (*Z*)-enol ether **17**. A subsequent control experiment revealed that this transformation requires only KOH and proceeds in the absence of [Mn] precatalyst **3**.^[23] Finally, 1-fluoro-4-nitrobenzene participated in a nucleophilic aromatic substitution (S_NAr) reaction with methanol to give **18** in 80% isolated yield. Employing ethanol as the solvent using otherwise “standard” reaction conditions, nitrobenzene was converted into aniline in 33% NMR yield with no *N*-ethylation observed.

A selection of further experiments were performed in order to gain insight into the mechanism of the reaction. Initially, it was found that azobenzene **19** and azoxybenzene **20** did not convert to *N*-methylaniline **2** when subjected to the optimized reaction conditions, which indicated that they are not productive intermediates (Scheme 3A).^[12,13] Conversely, >98% conversion to **2** was observed when aniline **21** was employed as the substrate. The reaction progress with time was monitored for the reductive methylation of nitrobenzene **1** (Scheme 3B).^[17] Product **2** was initially formed slowly, with only 7% conversion to **2** observed after 4 h, which may partly be due to the time required for activation of the [Mn] precatalyst **3** with KOH. The long induction period prompted us to explore the stability of the catalyst by monitoring the presence of carbonyl ligands using FT-IR during the course of the reaction.^[24] After 6 h reaction time, absorption bands corresponding to carbonyl ligands were observed.^[17] However, the formation of a heterogeneous active species cannot be excluded. Beyond 4 h, the rate of formation of **2** increased, with 58% conversion observed after 8 h. Conversion to **2** reached a maximum of 88% after 24 h, at which time no nitrobenzene **1** remained. The small quantities of aniline **21** observed (6% after 4 h and 3% after 8 h) supported a mechanism that involved an initial transfer hydrogenation followed by condensation and subsequent aldimine hydrogenation to form **2**. Dihydrogen and formaldehyde were detected *via* sampling the headspace of the reaction vessel and the reaction mixture, respectively.^[17] The reaction is selective for mono-*N*-methylation, with no dimethylated products observed.

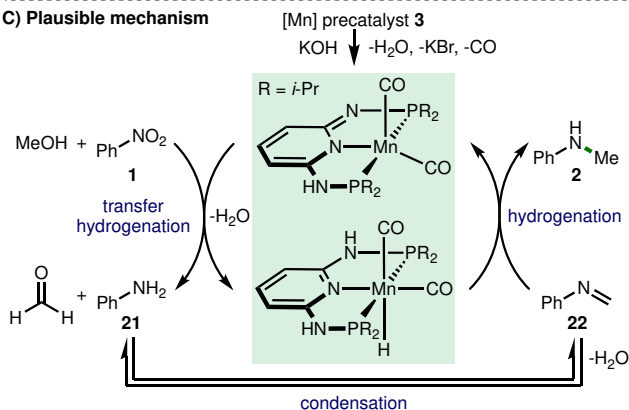
A) Validation of possible reaction intermediates



B) Time course experiment



C) Plausible mechanism



Scheme 3. Mechanistic Studies. [a] As determined by ¹H NMR analysis of the crude reaction mixture with 1,3,5-trimethylbenzene as the internal standard.

When CD₃OD or CD₃OH were employed as solvents using otherwise “standard” reaction conditions, nitrobenzene **1** was fully recovered. In line with these observations, and previous related investigations,^[15,16,19] a plausible reaction mechanism initiates with activation of [Mn] precatalyst **3** with KOH to form the active manganese complex (Scheme 3C). Subsequent transfer hydrogenation converts nitrobenzene **1** and methanol into aniline **21** and formaldehyde, which can undergo a condensation reaction to form *N*-phenylmethanimine **22**. Hydrogenation of **22** with the manganese hydride provides

access to the *N*-methylated product **2** with regeneration of the catalytically active species. *N*-Phenylmethanimine **22** was not observed during the time course experiment, which suggests that aldimine hydrogenation must occur rapidly using these reaction conditions.

Conclusions

In conclusion, we have developed a new synthetic method for the one-pot conversion of nitroarenes into *N*-methylarylamines. Mechanistic experiments suggest a transfer hydrogenation mechanism, which enabled methanol to be employed as both the methylating agent and the reductant. This is the first report that employs a well-defined organometallic complex based upon an earth-abundant first row transition metal for this transformation. Ongoing studies are focused on further applications of earth-abundant transition metals in synthetic organic chemistry and these results will be reported in due course.

Acknowledgements

We gratefully acknowledge the School of Chemistry, Cardiff University for generous support and the EPSRC Doctoral Training Grant for a partially funded PhD studentship (B.G.R.-B., EP/M507842/1).

Keywords: transfer hydrogenation • manganese catalysis • methanol • nitroarenes • *N*-methylanilines

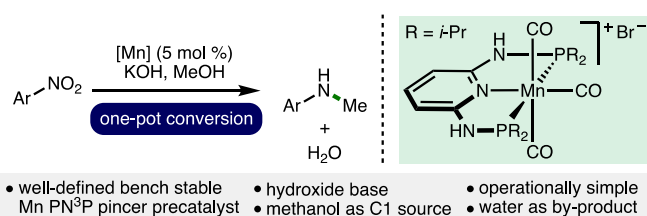
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- [24] We sincerely thank the reviewers for suggesting that we investigate the stability of the catalyst.
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Entry for the Table of Contents

Layout 2:

COMMUNICATION



Benjamin G. Reed-Berendt, Nicolas Mast, and Louis C. Morrill*

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Take the direct route!: A manganese-catalyzed one-pot conversion of nitroarenes into *N*-methylarylamines has been developed. This transfer hydrogenation method employs a well-defined bench stable Mn PN^3P pincer precatalyst in combination with methanol as both the reductant and the C1 source. A selection of commercially available nitroarenes was converted into *N*-methylarylamines in synthetically useful yields.